

Form PTO-1390US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE (Rev. 5-93) TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		ATTORNEY'S DOCKET NO H 4020 PCT/US U S APPLICATION NO. (if known sec 17 CFR 15) 10/048208
INTERNATIONAL APPLICATION NO. PCT/EP00/07163	INTERNATIONAL FILING DATE August 2, 2000	PRIORITY DATE CLAIMED August 5, 1999
TITLE OF INVENTION AGENT FOR DYING KERATIN FIBERS		
APPLICANT(S) FOR DO/EO/US Hinrich Moeller, Doris Oberkobusch, and Horst Hoeffkes,		
Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information:		
<p>1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).</p> <p>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <p>a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</p> <p><input checked="" type="checkbox"/> has been transmitted by the International Bureau.</p> <p><input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))</p> <p>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</p> <p>b. <input type="checkbox"/> have been transmitted by the International Bureau.</p> <p>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p>d. <input checked="" type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). UNEXECUTED</p> <p>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p>		
Items 11. to 16. below concern other document(s) or information included:		
<p>11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment</p> <p><input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</p> <p>14. <input type="checkbox"/> A substitute specification.</p> <p>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>16. <input checked="" type="checkbox"/> Other items or information.:.</p>		
Version with Markings to Show Changes Made; Information Disclosure Citation (Form PTO-1449) and References; and International Search Report		
<p>"Express Mail" mailing label number EL615774989US</p>		

U.S. Application No. (If known see CFR1.30) 10/048208	INTERNATIONAL APPLICATION NO. PCT/EP00/07163	ATTORNEY'S DOCKET NUMBER H 4020 PCT/US		
<p>17. <input checked="" type="checkbox"/> The following fees are submitted:</p> <p>Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO.....\$890.00</p> <p>International preliminary examination fee paid to USPTO (37CFR 1.482)\$710.00</p> <p>No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37CFR 1.445(a)(2))....\$740.00</p> <p>Neither international preliminary examination fee (37CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO. \$1,040.00</p> <p>International preliminary examination fee paid to USPTO (37CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4). \$100.00</p>		CALCULATIONS PTO USE ONLY		
ENTER APPROPRIATE BASIC FEE AMOUNT		= \$ 890 Order No. 02-0052 00		
<p>Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date 37 (CFR 1.492(e)).</p>		\$ 00		
<input type="checkbox"/> Claims	Number filed	Number Extra	Rate	
<input type="checkbox"/> Total Claims	21- 20 =1	1	X 18.00	\$ 18 Order No. 02-0066
<input type="checkbox"/> Independent Claims	2- 3 =1	0	X 84.00	\$ 00
Multiple dependent claims (s)(if applicable)		0	+ 280.00	\$ 00
TOTAL OF ABOVE CALCULATIONS		=	\$ 908	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).			\$ 00	
SUBTOTAL		=	\$ 908	
Processing fee of \$130.00 for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37CFR 1.492(f)).		+	\$ 00	
TOTAL NATIONAL FEE		=	\$ 908	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +			\$ 00	
TOTAL FEES ENCLOSED		=	\$ 908	
		Amount to be: refunded	\$ -----	
		charged		
<p>a. <input type="checkbox"/> A check in the amount of \$ _____ to cover the above fees is enclosed.</p> <p>b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>01-1250</u> in the amount of <u>\$ 890.00</u> to cover the above fees.</p> <p>A triplicate copy of this sheet is enclosed. Order No. _____</p> <p>c. <input checked="" type="checkbox"/> The Assistant Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>01-1250</u>. A triplicate copy of this sheet is enclosed.</p>				
<p>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.</p>				
<p>SEND ALL CORRESPONDENCE TO: Henkel Corporation, Law Dept. 2500 Renaissance Blvd., Ste. 200 Gulph Mills, PA 19406.....</p>				
<u>Kimberly R. Hild</u> SIGNATURE				
<p><u>Kimberly R. Hild</u> NAME ATTORNEY FOR APPLICANT 39,224</p>				
<p>REGISTRATION NUMBER</p>				

PATENT
Docket No. H 4020 PCT/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Moeller, et al.

International Application No. PCT/EP00/07163

International Filing Date: August 2, 2000

Serial No. To be assigned

Examiner: To be assigned

Filed: To be assigned

Art Unit: To be assigned

Title: AGENT FOR DYING KERATIN FIBERS

"Express Mail Post Office to Addressee" service mailing label number EL 615774989 US

PRELIMINARY AMENDMENT

Box PCT
Assistant Commissioner for Patents
Washington, DC 20231

Attn: DO/EO/US

Sir:

Prior to examining this application, please amend the application as follows:

In the Specification (Using the English Translation):

On page 1 of the English translation, on a separate line between the title and line 1, please insert the following paragraph:

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-- CROSS REFERENCE TO RELATED APPLICATIONS

This application is a national stage application under 35 U.S.C. §371 of international application PCT/EP00/07163 filed on August 2, 2000, the international application not being published in English. This application also claims priority under 35 U.S.C. §119 to DE 199 36 911.9 filed on August 5, 1999. --

On page 1, on a separate line after the above inserted paragraph and before line 1, please insert the following header:

-- BACKGROUND OF THE INVENTION -- .

On page 3, on a separate line between lines 11 and 12, please insert the following header:
--SUMMARY OF THE INVENTION--.

On page 5, on a separate line between lines 17 and 18, please insert the following header:
-- DETAILED DESCRIPTION OF THE INVENTION --.

On page 27, line 1, please delete the heading “CLAIMS” and insert therefor:
-- What is claimed is: --

On a separate page, after page 36, please insert the enclosed Abstract of the Disclosure.

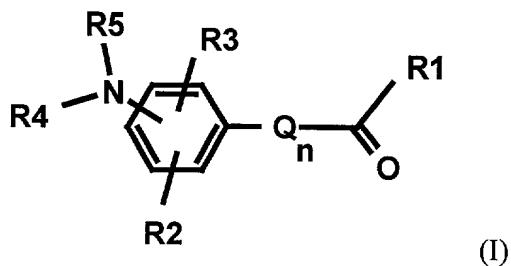
In the Claims

Please cancel Claims 1 to 13, without prejudice.

Please add the following new claims:

-- 14. (NEW) A composition for coloring keratin-containing fibers comprising a mixture of, or a reaction product of, or both of:

(A) at least one aromatic aldehyde or ketone corresponding to formula I:



wherein R¹ represents a hydrogen atom, a C₁₋₄ alkyl group or an aryl group,

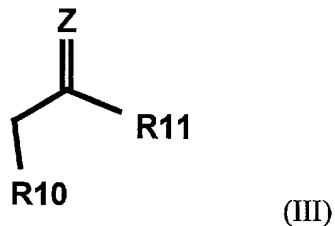
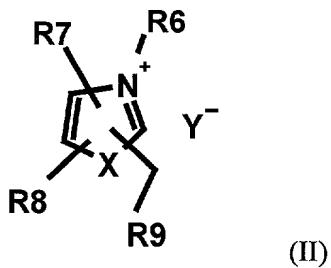
wherein R² and R³, independently of one another, represent a hydrogen atom, a C₁₋₄ alkyl group, a halogen atom, a hydroxy group, a C₁₋₄ alkoxy group or a nitro group, or R² and R³ together form a fused aromatic ring,

wherein R⁴ and R⁵, independently of one another, represent a hydrogen atom, a C₁₋₄ alkyl group, a C₂₋₄ hydroxyalkyl group, a C₁₋₄ alkenyl group or aryl group, or R⁴ and R⁵ together with the nitrogen atom form a five- to seven-membered heterocyclic ring, or one of R⁴ or R⁵ forms a saturated or unsaturated 5-, 6- or 7-membered ring with one of the substituents R² or R³,

wherein Q is a direct bond, a vinylene group or vinylidene group, wherein the vinylene group or vinylidene group may optionally together with one of the two substituents R⁴ or R⁵, form an indole ring or an indoline ring, and

wherein n is 1 or 2; and

(B) one or more CH-active compounds corresponding to formula II, formula III, or mixtures thereof:



wherein R⁶ represents a C₁₋₁₀ alkyl group, a C₂₋₁₀ alkenyl group, a C₂₋₄ hydroxyalkyl group, a C₂₋₄ carboxyalkyl group, a C₂₋₄ sulfoalkyl group or an aralkyl group,

wherein R⁷ and R⁸, independently of one another, represent a hydrogen atom, a C₁₋₄ alkyl group, a halogen atom, a hydroxy group, a C₁₋₄ alkoxy group or a nitro group, or R⁷ and R⁸ together form a fused aromatic ring,

wherein R⁹ represents a hydrogen atom, a C₁₋₄ alkyl group or an aryl group,

wherein X is an oxygen atom or sulfur atom, a >N-R¹² group or -CH=CH- group, where R¹² is a C₁₋₄ alkyl group, a C₂₋₄ carboxyalkyl group, a C₂₋₄ sulfoalkyl group, a C₂₋₄ sulfoxalkyl group, a C₂₋₄ hydroxyalkyl group or an aralkyl group,

wherein Y⁻ represents an anion selected from a halide, a C₁₋₄ alkyl sulfate, a C₁₋₄ alkane sulfonate, an arene sulfonate, a C₁₋₄ perfluoroalkanesulfonate, a tetrafluoroborate, a perhalogenate, a sulfate, a hydrogen sulfate or a carboxylate,

wherein R¹⁰ represents a C₁₋₄ acyl group, an aroyl group, a C₁₋₄ alkylsulfonyl group, a C₁₋₄ alkylsulfinyl group, a C₁₋₄ alkylamino group, a di-C₁₋₄-alkylamino group, a vinylcarbonyl group, a methineimino group, a nitrile group, an ester or a carboxylic acid amide group, the carboxylic acid amide group being optionally substituted by one or more C₁₋₄ alkyl, C₂₋₄ hydroxyalkyl or aryl groups,

wherein R¹¹ represents a C₁₋₄ acyl group, a C₁₋₄ alkoxy group, a C₁₋₄ alkylamino group, a C₁₋₄ acylamino group or a di-C₁₋₄-alkylamino group, or wherein the substituents R¹⁰ and R¹¹ together with the rest of the molecule form a 5-, 6- or 7-membered heterocycle selected from 1,3-thiazolidine-2,5-dione, 1,3-thiazolidine-2-thione-5-one, perhydropyrimidine-2,4,6-trione, perhydropyrimidine-2-thione-4,6-dione, cyclopentane-1,3-dione, cyclohexane-1,3-dione, indole, indan-1,3-dione, indan-1-one, 2-pyrazoline-5-one, 1,2-dihydro-6-hydroxy-2-hydroxypyridine or an enol ester derivative of the 5- to 7-membered heterocycle, and

wherein Z represents oxygen, sulfur or a dicyanomethylene group.

15. (NEW) The composition of claim 14 wherein the aromatic aldehyde or ketone of formula I comprises a compound selected from 4-dimethylaminobenzaldehyde, 4-diethylaminobenzaldehyde, 4-dimethylamino-2-hydroxybenzaldehyde, 4-pyrrolidinobenzaldehyde, 4-morpholinobenzaldehyde, 4-piperidinobenzaldehyde, 4-dimethylaminoacetophenone, 4-dimethylaminonaphthaldehyde, 4-dimethylaminobenzylidene acetone, 4-dimethylamino cinnamaldehyde, 2-dimethylaminobenzaldehyde, 2-chloro-4-dimethylaminobenzaldehyde, 4-dimethylamino-2-methylbenzaldehyde, trans-4-diethylaminocinnamaldehyde, 4-(dibutylamino)-benzaldehyde, 4-diphenylaminobenzaldehyde, 2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinoxiline-9-carboxaldehyde, 4-dimethylamino-2-methoxybenzaldehyde, 2,3,6,7-tetrahydro-8-hydroxy-1H,5H-benzo[ij]quinoxiline-9-carboxaldehyde, 4-(1-imidazolyl)-benzaldehyde, 2-morpholinobenzaldehyde, indole-3-carboxaldehyde, 1-methylindole-3-carboxaldehyde, N-ethylcarbazole-3-aldehyde, 2-formylmethylene-1,3,3-trimethylindoline or mixtures thereof.

16. (NEW) The composition of claim 14, wherein the composition comprises a compound corresponding to formula II selected from a salt of 1,4-dimethylquinolinium, 1,2-dimethylquinolinium, 1,4-dimethylpyridinium, 1,2-dimethylpyridinium, 2-methyl-1-ethylquinolinium, 2,3-dimethylisoquinolinium, 1,2,3,3-tetramethyl-3H-indolinium, 2,3-dimethylbenzothiazolium, 2,3-dimethyl-6-nitrobenzothiazolium, 3-benzyl-2-benzothiazolium, 2-methyl-3-propyl benzothiazolium, 2,4-dimethyl-3-ethylthiazolium, 3-(2-carboxyethyl)-2,5-dimethylbenzothiazolium, 1,2,3-trimethylbenzimidazolium, 5,6-dichloro-1,3-diethyl-2-methyl benzimidazolium, 3-ethyl-2-methylbenzothiazolium, 3-ethyl-2-methylnaphtho[1,2-d]thiazolium, 5-chloro-3-ethyl-2-methylbenzothiazolium, or 3-ethyl-2-methyl benzoxazolium, or 2-methyl-3-(3-sulfopropyl)-benzothiazolium hydroxide or an inner salt thereof, or 5-methoxy-2-methyl-3-(3-sulfopropyl)-benzothiazolium hydroxide or an inner salt thereof, or mixtures of any of the foregoing compounds corresponding to formula II.

17. (NEW) The composition of claim 16 wherein Y⁻ of the salt comprises one or more chlorides, bromides, iodides, methanesulfonates, benzenesulfonates, p-toluenesulfonates, trifluoromethane sulfonates, methyl sulfates, tetrafluoroborates, or mixtures thereof.

18. (NEW) The composition of claim 14, wherein the composition comprises a compound corresponding to formula III selected from rhodanine, rhodanine-3-acetic acid, barbituric acid, thiobarbituric acid, 1,3-dimethyl thiobarbituric acid, 1,3-diethyl thiobarbituric acid, oxindole, 3-indoxyl acetate, coumaranone, 1-methyl-3-phenylpyrazolinone, indan-1,3-dione, cyclopentane-1,3-dione, 1,2-dihydro-1-ethyl-6-hydroxy-4-methyl-2-oxo-3-pyridinecarbonitrile or mixtures thereof.

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19. (NEW) The composition of claim 14 wherein the composition comprises a reaction of the aromatic aldehyde or ketone of formula I and the CH-active compound, and the reaction product is selected from Quinaldine Red (2-[4-(dimethylamino)-styryl]-1-ethyl quinolinium iodide), 2-[4-(dimethylamino)-styryl]-1-methyl quinolinium iodide, 2-[4-dimethylamino)-styryl]-1-ethylpyridinium iodide, 2-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide, 4-[4-dimethylaminostyryl]-1-methyl pyridinium tosylate, 4-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizin-9-yl)-ethenyl]-1-methylpyridinium iodide, trans-4-[4-(dibutylamino)-styryl]-1-methyl pyridinium iodide, 2,6-bis-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide, 2-[4-(dimethylamino)-styryl]-3-methyl benzoxazolium perchlorate, 2-[4-(dimethylamino)-styryl]-3-methyl benzoxazolium iodide, or 2-[4-(dimethylamino)-styryl-1-ethylnaphthol[1,2-d]thiazolium iodide or mixtures thereof.

20. (NEW) The composition of claim 14, wherein the aromatic aldehyde or ketone corresponding to formula I and the compound of formula II or formula III are each present in the composition in an amount of 0.03 mmol to 65 mmol, based on 100 grams of the composition as a whole.

21. (NEW) The composition of claim 20, wherein the aromatic aldehyde or ketone corresponding to formula I and the compound of formula II or formula III are each present in the composition in an amount of 1 mmol to 40 mmol, based on 100 grams of the composition as a whole.

22. (NEW) The composition of claim 14, further comprising one or more color intensifiers selected from piperidine, piperidine-2-carboxylic acid, piperidine-3-carboxylic acid, piperidine-4-carboxylic acid, pyridine, 2-hydroxypyridine, 3-hydroxypyridine, 4-hydroxypyridine, imidazole, 1-methyl imidazole, histidine, pyrrolidine, proline, pyrrolidone, pyrrolidone-5-carboxylic acid, pyrazole, 1,2,4-triazole or piperazidine, or mixtures thereof.

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23. (NEW) The composition of claim 14 further comprising from 0.01 weight percent to 20 weight percent, based on the total weight of the composition, of one or more substantive dyes selected from nitrophenylenediamines, nitroaminophenols, anthraquinones or indophenols, or combinations thereof.

24. (NEW) The composition of claim 14 further comprising one or more ammonium or metal salts selected from formates, carbonates, halides, sulfates, butyrates, valerates, caproates, acetates, lactates, glycolates, tartrates, citrates, gluconates, propionates, phosphates or phosphonates or combinations thereof.

25. (NEW) The composition of claim 24 wherein the cationic component of the ammonium or metal salts comprises one or more ammonium ions, alkali metals, alkaline earth metals, aluminum, manganese, iron, cobalt, copper or zinc or mixtures thereof.

26. (NEW) The composition of claim 14 further comprising one or more oxidizing agents.

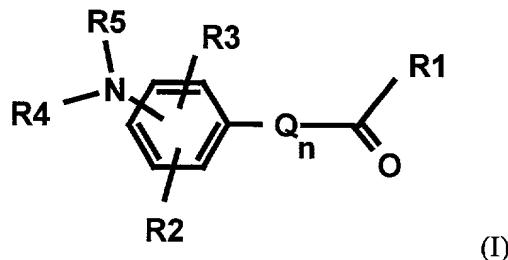
27. (NEW) The composition of claim 26 wherein the oxidizing agents comprise from 0.01 weight percent to 6 weight percent H₂O₂, based on the total weight of the composition.

28. (NEW) The composition of claim 14, further comprising one or more anionic, zwitterionic or nonionic surfactants, or combinations thereof.

29. (NEW) A method for coloring keratin-containing fibers comprising applying the composition of claim 14 to keratin-containing fibers.

30. (NEW) A process for coloring keratin-containing fibers comprising applying to keratin containing fibers

(a) at least one aromatic aldehyde or ketone corresponding to formula I:



wherein R¹ represents a hydrogen atom, a C₁₋₄ alkyl group or an aryl group,

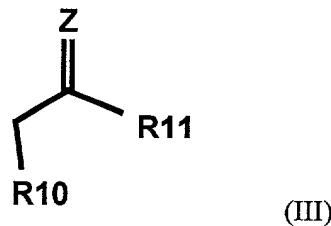
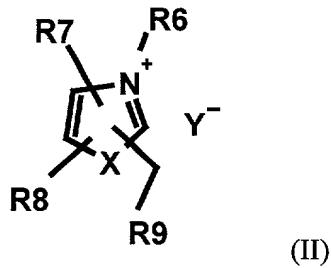
wherein R² and R³, independently of one another, represent a hydrogen atom, a C₁₋₄ alkyl group, a halogen atom, a hydroxy group, a C₁₋₄ alkoxy group or a nitro group, or R² and R³ together form a fused aromatic ring,

wherein R⁴ and R⁵, independently of one another, represent a hydrogen atom, a C₁₋₄ alkyl group, a C₂₋₄ hydroxyalkyl group, a C₁₋₄ alkenyl group or aryl group, or R⁴ and R⁵ together with the nitrogen atom form a five- to seven-membered heterocyclic ring, or one of R⁴ or R⁵ forms a saturated or unsaturated 5-, 6- or 7-membered ring with one of the substituents R² or R³,

wherein Q is a direct bond, a vinylene group or vinylidene group, wherein the vinylene group or vinylidene group may optionally together with one of the two substituents R⁴ or R⁵, form an indole ring or an indoline ring, and

wherein n is 1 or 2; and

(b) one or more CH-active compounds corresponding to formula II, formula III or mixtures thereof:



wherein R⁶ represents a C₁₋₁₀ alkyl group, a C₂₋₁₀ alkenyl group, a C₂₋₄ hydroxyalkyl group, a C₂₋₄ carboxyalkyl group, a C₂₋₄ sulfoalkyl group or an aralkyl group,

wherein R⁷ and R⁸, independently of one another, represent a hydrogen atom, a C₁₋₄ alkyl group, a halogen atom, a hydroxy group, a C₁₋₄ alkoxy group or a nitro group, or R⁷ and R⁸ together form a fused aromatic ring,

wherein R⁹ represents a hydrogen atom, a C₁₋₄ alkyl group or an aryl group,

wherein X is an oxygen atom or sulfur atom, a >N-R¹² group or -CH=CH- group, where R¹² is a C₁₋₄ alkyl group, a C₂₋₄ carboxyalkyl group, a C₂₋₄ sulfoalkyl group, a C₂₋₄ sulfoxalkyl group, a C₂₋₄ hydroxyalkyl group or an aralkyl group,

wherein Y⁻ represents an anion selected from a halide, a C₁₋₄ alkyl sulfate, a C₁₋₄ alkane sulfonate, an arene sulfonate, a C₁₋₄ perfluoroalkanesulfonate, a tetrafluoroborate, a perhalogenate, a sulfate, a hydrogen sulfate or a carboxylate,

wherein R¹⁰ represents a C₁₋₄ acyl group, an aroyl group, a C₁₋₄ alkylsulfonyl group, a C₁₋₄ alkylsulfinyl group, a C₁₋₄ alkylamino group, a di-C₁₋₄-alkylamino group, a vinylcarbonyl group, a methineimino group, a nitrile group, an ester or a carboxylic acid amide group, the carboxylic acid amide group being optionally substituted by one or more C₁₋₄ alkyl, C₂₋₄ hydroxyalkyl or aryl groups,

wherein R¹¹ represents a C₁₋₄ acyl group, a C₁₋₄ alkoxy group, a C₁₋₄ alkylamino group, a C₁₋₄ acylamino group or a di-C₁₋₄-alkylamino group, or wherein the substituents R¹⁰ and R¹¹ together with the rest of the molecule form a 5-, 6- or 7-membered heterocycle selected from 1,3-thiazolidine-2,5-dione, 1,3-thiazolidine-2-thione-5-one, perhydropyrimidine-2,4,6-trione, perhydropyrimidine-2-thione-4,6-dione, cyclopentane-1,3-dione, cyclohexane-1,3-dione, indole, indan-1,3-dione, indan-1-one, 2-pyrazoline-5-one, 1,2-dihydro-6-hydroxy-2-hydroxypyridine or an enol ester derivative of the 5- to 7-membered heterocycle, and

wherein Z represents oxygen, sulfur or a dicyanomethylene group.

31. (NEW) The method of claim 30 wherein the aromatic aldehyde or ketone of formula I and the CH-active compound are applied simultaneously or successively in any order to the keratin-containing fibers.

32. (NEW) The method of claim 30 wherein the aromatic aldehyde or ketone and the CH-active compound are formulated into a coloring composition prior to the applying step.

33. (NEW) The method of claim 32 wherein the coloring composition comprises a reaction product of the aromatic aldehyde or ketone and the CH-active compound.

34. (NEW) The method of claim 30 wherein the keratin-containing fiber is hair, and following the applying step, the aromatic aldehyde or ketone and the CH-active compound are washed out with a shampoo or rinsed out from the hair after a contact time of about 30 minutes. --

REMARKS

Applicants respectfully request the Examiner to enter the above amendments prior to examination of this application.

Status of Claims

Claims 14 to 34 will be pending after entry of the present amendment. Claims 1 to 13 are being canceled without prejudice.

Amendment

The specification is being amended to insert section headers and an abstract of the disclosure in accordance with 37 CFR §1.77 to better conform with US patent practice. The specification is also being amended to insert a cross-reference to related applications in accordance 37 CFR §1.78 and to claim priority to those applications listed therein.

Attached hereto is a marked up version of the changes made to the specification entitled "Version With Markings To Show Changes Made."

New Claims 14 to 34 replace original claims 1 to 13, and are being presented to better conform with US patent practice. These new claims are supported by the specification for example as shown in the Table below (cites to the specification are for the English translation):

Claim	Support in Specification
14	page 3, line 12 to page 5, line 17
15	page 5, line 26 to page 6, line 10
16, 17	page 6, lines 11 to 26
18	page 6, line 27 to page 7, line 2
19	page 7, lines 3 to 14
20, 21	page 7, lines 17 to 22
22	page 7, line 26 to page 8, line 3
23	page 8, line 17 to page 9, line 3
24, 25	page 16, lines 11 to 22
26, 27	page 8, lines 10 to 16
28	page 9, lines 24 to 30

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Claim	Support in Specification
29, 30, 31, 34	page 16, line 25 to page 21, line 19
32, 33	page 21, lines 20 to 27, page 22, lines 1 to 16

No new matter is added by the new claims or amendments to the specification.

CONCLUSION

Applicants respectfully request early and favorable notification of allowance of all pending claims. The Assistant Commissioner is authorized to charge any deficiency in the required fee or to credit any overpayment to Deposit Account 01-1250 in connection with this amendment.

Respectfully submitted,

Kimberly R. Hild
Kimberly R. Hild
(Reg. No. 39,224)
Attorney for Applicants
(610) 278-4964

Henkel Corporation
Law Department
2500 Renaissance Boulevard, Suite 200
Gulph Mills, PA 19406

Abstract of the Disclosure

A coloring composition and a method of coloring keratin-containing fibers are provided. The coloring composition contains a mixture of and/or a reaction product of at least one aromatic aldehyde or ketone and at least one CH-active compound. In the method of the present invention, the aromatic aldehyde or ketone and the CH-active compound may be applied to keratin-containing fibers simultaneously or successively.

Agent for Dying Keratin Fibers

This invention relates to a composition for coloring keratin fibers, more particularly human hair, which contains a combination of aromatic aldehydes or ketones and CH-active compounds, to the use of this combination as a coloring component in hair colorants and to a process for coloring keratin-containing fibers, more particularly human hair.

In general, keratin-containing fibers, for example hair, wool or pelts, are dyed either with substantive dyes or with oxidation dyes which are formed by oxidative coupling of one or more primary intermediates with one another or with one or more secondary intermediates. Primary and secondary intermediates are also known as oxidation dye precursors.

The primary intermediates normally used are primary aromatic amines containing another free or substituted hydroxy or amino group in the para or ortho position, diaminopyridine derivatives, heterocyclic hydrazones, 4-aminopyrazolone derivatives and 2,4,5,6-tetraaminopyrimidine and derivatives thereof.

Special representatives are, for example, p-phenylenediamine, p-toluylenediamine, 2,4,5,6-tetraaminopyrimidine, p-aminophenol, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine, 2-(2,5-diaminophenyl)-ethanol, 2-(2,5-diaminophenoxy)-ethanol, 1-phenyl-3-carboxyamido-4-amino-5-pyrazolone, 4-amino-3-methylphenol, 2-aminomethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6-triamino-4-hydroxypyrimidine.

The secondary intermediates used are generally m-phenylenediamine derivatives, naphthols, resorcinol and resorcinol derivatives, pyrazolones, m-aminophenols and substituted pyridine derivatives. Particularly suitable secondary intermediates are α -naphthol, 1,5-, 2,7- and 1,7-dihydroxynaphthalene, 5-amino-2-methylphenol, m-aminophenol,

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resorcinol, resorcinol monomethyl ether, m-phenylenediamine, 2,4-diaminophenoxyethanol, 2-amino-4-(2-hydroxyethylamino)-anisole (Lehmann's blue), 1-phenyl-3-methyl-5-pyrazolone, 2,4-dichloro-3-aminophenol, 1,3-bis-(2,4-diaminophenoxy)-propane, 2-chlororesorcinol, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methyl resorcinol, 5-methyl resorcinol, 3-amino-6-methoxy-2-methylaminopyridine and 3,5-diamino-2,6-dimethoxypyridine.

With regard to other typical dye components, reference is specifically made to the series entitled "**Dermatology**" (Editors: Ch. Culnan and H. Maibach), Marcel Dekker Inc., New York/Basel, 1986, Vol. 7, Ch. Zviak, **The Science of Hair Care**, Chapter 7 (pages 248-250; Substantive Dyes) and Chapter 8 (pages 264-267; Oxidation Dye Precursors) and to the "**Europäische Inventar der Kosmetik-Rohstoffe**" published by the European Commission and available on floppy disk from the Bundesverband Deutscher Industrie- und Handelsunternehmen für Arzneimittel, Reformwaren und Körperpflegemittel e.V., Mannheim, Germany.

Although intensive colors with good fastness properties can be obtained with oxidation dyes, the color is generally developed under the influence of oxidizing agents, such as H_2O_2 for example, which in some cases can result in damage to the fibers. In addition, some oxidation dye precursors or certain mixtures of oxidation dye precursors can occasionally have a sensitizing effect in people with sensitive skin. Although substantive dyes are applied under more moderate conditions, their disadvantage is that, in many cases, the colors obtained often have inadequate fastness properties.

The use of the combination of aromatic aldehydes or ketones and CH-active compounds described hereinafter for coloring keratin-containing fibers has not hitherto been known.

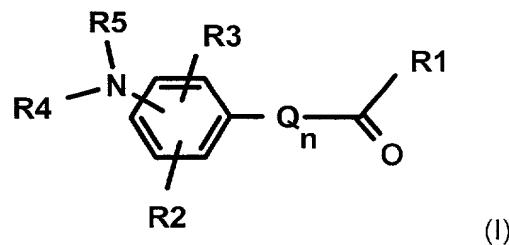
The problem addressed by the present invention was to provide colorants for keratin fibers, more especially human hair, which would be at

least equivalent in quality to conventional oxidation hair dyes in regard to depth of color, grey coverage and fastness properties, but which would not necessarily have to contain oxidizing agents, such as H₂O₂ for example. In addition, the colorants according to the invention would have very little, if 5 any, sensitizing potential.

It has surprisingly been found that the combination of the aromatic aldehydes or ketones represented in formula I and CH-active compounds corresponding to formulae II and/or III is eminently suitable for coloring keratin-containing fibers, even in the absence of oxidizing agents. They 10 give colors with excellent brilliance and depth of color and lead to a wide variety of shades. In principle, however, oxidizing agents may be present.

The present invention relates to a composition for coloring keratin-containing fibers, more particularly human hair, containing a combination of aromatic aldehydes or ketones corresponding to formula I:

15



in which

R¹ is a hydrogen atom, a C₁₋₄ alkyl or an aryl group,

20 R² and R³ independently of one another represent a hydrogen atom, a C₁₋₄ alkyl group, a halogen atom, a hydroxy, C₁₋₄ alkoxy or nitro group or together form a fused aromatic ring,

R⁴ and R⁵ represent a hydrogen atom, a C₁₋₄ alkyl, C₂₋₄ hydroxyalkyl, C₁₋₄ alkenyl or aryl group or, together with the nitrogen atom, form a five- to

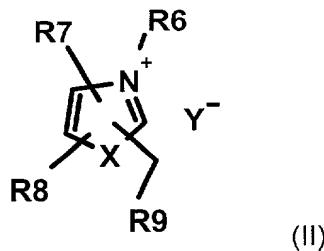
25 seven-membered heterocyclic ring or one of them forms a saturated or unsaturated 5-, 6- or 7-membered ring with one of the substituents R² or

R^3 ,

Q is a direct bond or a vinylene or vinylidene group which, together with one of the two substituents R^4 or R^5 , may form an indole ring or - where an exocyclic double bond is formed - an indoline ring and

5 $n = 1$ or 2 ,

and CH-active compounds corresponding to formulae II and/or III:



10 in which

R^6 is a C_{1-10} alkyl, C_{2-10} alkenyl, C_{2-4} hydroxyalkyl, C_{2-4} carboxyalkyl, C_{2-4} sulfoalkyl or aralkyl group,

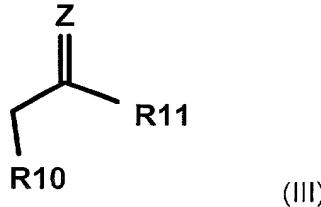
R^7 and R^8 independently of one another represent a hydrogen atom, a C_{1-4} alkyl group, a halogen atom, a hydroxy, C_{1-4} alkoxy or nitro group or

15 together form a fused aromatic ring,

R^9 represents a hydrogen atom, a C_{1-4} alkyl or an aryl group,

X is an oxygen or sulfur atom, the group $>N-R^{12}$ or $-CH=CH-$, where R^{12} is a C_{1-4} alkyl, C_{2-4} carboxyalkyl, C_{2-4} sulfoalkyl, C_{2-4} sulfoxyalkyl, C_{2-4} hydroxyalkyl or aralkyl group, and

20 Y^- is an anion selected from halide, C_{1-4} alkyl sulfate, C_{1-4} alkane sulfonate, arene sulfonate, C_{1-4} perfluoroalkanesulfonate, tetrafluoroborate, perhalogenate, sulfate, hydrogen sulfate or carboxylate,



in which

R^{10} is a C_{1-4} acyl group, aroyl, C_{1-4} alkylsulfonyl, C_{1-4} alkylsulfinyl, C_{1-4} alkylamino, di- C_{1-4} -alkylamino, vinylcarbonyl, methineimino, nitrile, ester or carboxylic acid amide group which may optionally be substituted by C_{1-4}

5 alkyl, C_{2-4} hydroxyalkyl or aryl groups and

R^{11} is a C_{1-4} acyl, C_{1-4} alkoxy, C_{1-4} alkylamino, C_{1-4} acylamino or di- C_{1-4} -alkylamino group,

the substituents R^{10} and R^{11} together with the rest of the molecule forming a 5-, 6- or 7-membered heterocycle from the series of 1,3-thiazolidine-2,5-

10 diones, 1,3-thiazolidine-2-thione-5-ones, perhydropyrimidine-2,4,6-triones, perhydropyrimidine-2-thione-4,6-diones, cyclopentane-1,3-diones, cyclohexane-1,3-diones, indolines, indan-1,3-diones, indan-1-ones, 2-pyrazoline-5-ones, 1,2-dihydro-6-hydroxy-2-hydroxypyridines or enol esters thereof, and

15 Z represents oxygen, sulfur or the dicyanomethylene group, and/or reaction products of the compounds corresponding to formulae I and II and/or III.

In the context of the invention, keratin-containing fibers are understood to include wool, pelts, feathers and, in particular, human hair.

20 In principle, however, the colorants according to the invention may also be used to color other natural fibers such as, for example, cotton, jute, sisal, linen or silk, modified natural fibers such as, for example, regenerated cellulose, nitro, alkyl or hydroxyalkyl or acetyl cellulose and synthetic fibers such as, for example, polyamide, polyacrylonitrile, polyurethane and 25 polyester fibers.

Preferred compounds corresponding to formula I are, for example, 4-dimethylaminobenzaldehyde, 4-diethylaminobenzaldehyde, 4-dimethylamino-2-hydroxybenzaldehyde, 4-pyrrolidinobenzaldehyde, 4-morpholino-benzaldehyde, 4-piperidinobenzaldehyde, 4-dimethylaminoacetophenone, 30 4-dimethylaminonaphthaldehyde, 4-dimethylaminobenzylidene acetone, 4-

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dimethylamino cinnamaldehyde, 2-dimethylaminobenzaldehyde, 2-chloro-4-dimethylaminobenzaldehyde, 4-dimethylamino-2-methylbenzaldehyde, trans-4-diethylaminocinnamaldehyde, 4-(dibutylamino)-benzaldehyde, 4-diphenylaminobenzaldehyde, 2,3,6,7-tetrahydro-1H,5H-benzo[ij]quino-
5 ziline-9-carboxaldehyde, 4-dimethylamino-2-methoxybenzaldehyde, 2,3,6,7-tetrahydro-8-hydroxy-1H,5H-benzo[ij]quinoziline-9-carboxaldehyde, 4-(1-imidazolyl)-benzaldehyde, 2-morpholinobenzaldehyde, indole-3-carboxaldehyde, 1-methylindole-3-carboxaldehyde, N-ethylcarbazole-3-aldehyde, 2-formylmethylen-1,3,3-trimethylindoline (Fischer's aldehyde or
10 tribase aldehyde) and mixtures thereof.

Examples of preferred compounds corresponding to formula II are 1,4-dimethylquinolinium, 1,2-dimethylquinolinium, 1,4-dimethylpyridinium, 1,2-dimethylpyridinium, 2-methyl-1-ethylquinolinium, 2,3-dimethylisoquinolinium, 1,2,3,3-tetramethyl-3H-indolinium, 2,3-dimethylbenzothiazolium, 2,3-dimethyl-6-nitrobenzothiazolium, 3-benzyl-2-benzothiazolium, 2-methyl-3-propyl benzothiazolium, 2,4-dimethyl-3-ethylthiazolium, 3-(2-carboxyethyl)-2,5-dimethylbenzothiazolium, 1,2,3-trimethylbenzimidazolium, 5,6-dichloro-1,3-diethyl-2-methylbenzimidazolium, 3-ethyl-2-methylbenzothiazolium, 3-ethyl-2-methylnaphtho[1,2-d]thiazolium, 5-chloro-3-ethyl-2-methylbenzothiazolium, 3-ethyl-2-methyl benzoxazolium salts which may be present, for example, as chlorides, bromides, iodides, methanesulfonates, benzenesulfonates, p-toluenesulfonates, trifluoromethane sulfonates, methyl sulfates, tetrafluoroborates and 2-methyl-3-(3-sulfopropyl)-benzothiazolium hydroxide,
15 inner salt, 5-methoxy-2-methyl-3-(3-sulfopropyl)-benzothiazolium hydroxide, inner salt and mixtures of the above.

Examples of compounds corresponding to formula III are rhodanine, rhodanine-3-acetic acid, barbituric acid, thiobarbituric acid, 1,3-dimethyl and 1,3-diethyl thiobarbituric acid, oxindole, 3-indoxyl acetate, 30 coumaranone, 1-methyl-3-phenylpyrazolinone, indan-1,3-dione,

cyclopentane-1,3-dione, 1,2-dihydro-1-ethyl-6-hydroxy-4-methyl-2-oxo-3-pyridinecarbonitrile and mixtures of the above.

Examples of reaction products of the compounds corresponding to formulae I and II and/or III are Quinaldine Red (2-[4-(dimethylamino)-styryl]-

5 1-ethyl quinolinium iodide), 2-[4-(dimethylamino)-styryl]-1-methyl quinolinium iodide, 2-[4-(dimethylamino)-styryl]-1-ethylpyridinium iodide, 2-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide, 4-[4-dimethylaminostyryl]-1-methyl pyridinium tosylate, 4-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[*ij*]quinolizin-9-yl)-ethenyl]-1-methylpyridinium iodide, trans-4-[4-(dibutylamino)-styryl]-1-methyl pyridinium iodide and 2,6-bis-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide, 2-[4-(dimethylamino)-styryl]-3-methyl benzoxazolium perchlorate, 2-[4-(dimethylamino)-styryl]-3-methyl benzoxazolium iodide, 2-[4-(dimethylamino)-styryl]-1-ethylnaphthol[1,2-d]thiazolium iodide.

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15 These compounds are largely known from the literature or are commercially obtainable or may be obtained by known syntheses.

The above-mentioned compounds corresponding to formula I, formula II and formula III are used in the compositions according to the invention in quantities of preferably 0.03 to 65 mmol and more preferably 1 to 40 mmol, based on 100 g of the colorant as a whole. They may be used as substantive colorants or in the presence of typical oxidation dye precursors.

Colorants which contain the combination according to the invention as sole coloring component are preferably used for colors in the yellow, orange, red and violet range.

In order to obtain further and more intensive colors, the colorants according to the invention may additionally contain color intensifiers. The color intensifiers are preferably selected from the group consisting of piperidine, piperidine-2-carboxylic acid, piperidine-3-carboxylic acid, piperidine-4-carboxylic acid, pyridine, 2-hydroxypyridine, 3-hydroxypyridine,

4-hydroxypyridine, imidazole, 1-methyl imidazole, histidine, pyrrolidine, proline, pyrrolidone, pyrrolidone-5-carboxylic acid, pyrazole, 1,2,4-triazole, piperazidine, derivatives and physiologically compatible salts thereof.

The color intensifiers mentioned above may be used in a quantity of

5 0.03 to 65 and more particularly 1 to 40 mmol, based on 100 g of the colorant as a whole.

Various combinations of the compounds corresponding to formula I, II and/or III may also be used together in all colorants. Similarly, various color intensifiers may also be used together.

10 Oxidizing agents, for example H_2O_2 , need not be present. However, it may be desirable in some cases to add hydrogen peroxide or other oxidizing agents to the compositions according to the invention to obtain shades which are lighter than the keratin-containing fibers to be colored.

15 Oxidizing agents are generally used in a quantity of 0.01 to 6% by weight, based on the solution applied. A preferred oxidizing agent for human hair is H_2O_2 .

In one preferred embodiment, the colorants according to the invention contain typical substantive dyes, for example from the group of nitrophenylenediamines, nitroaminophenols, anthraquinones or indophenols, in addition to the compounds present in accordance with the invention in order further to modify the color tones. Examples of suitable substantive dyes are the compounds known under the International names or commercial names of HC Yellow 2, HC Yellow 4, HC Yellow 6, Basic Yellow 57, Disperse Orange 3, HC Red 3, HC Red BN, Basic Red 76, HC Blue 2, Disperse Blue 3, Basic Blue 99, HC Violet 1, Disperse Violet 1, Disperse Violet 4, Disperse Black 9, Basic Brown 16 and Basic Brown 17 and also picramic acid, 2-amino-6-chloro-4-nitrophenol, 4-amino-2-nitrodiphenylamine-2'-carboxylic acid, 6-nitro-1,2,3,4-tetrahydroquinoxaline, 4-N-ethyl-1,4-bis-(2'-hydroxyethylamino)-2-nitrobenzene hydrochloride and

30 1-methyl-3-nitro-4-(2'-hydroxyethyl)-aminobenzene. The compositions

according to the invention in this embodiment contain the substantive dyes in a quantity of, preferably, 0.01 to 20% by weight, based on the colorant as a whole.

In addition, the compositions according to the invention may also contain naturally occurring dyes such as, for example, henna red, henna neutral, henna black, camomile blossom, sandalwood, black tea, black alder bark, sage, logwood, madder root, catechu, sedre and alkanet.

Compounds I and II present in accordance with the invention or the color intensifiers and substantive dyes optionally present do not have to be

10 single compounds. Instead, the hair colorants according to the invention - due to the processes used for producing the individual dyes - may contain small quantities of other components providing they do not adversely affect the coloring result or have to be ruled out for other reasons, for example toxicological reasons.

15 The colorants according to the invention produce intensive colors even at physiologically compatible temperatures of <45°C. Accordingly, they are particularly suitable for coloring human hair. For application to human hair, the colorants are normally incorporated in a water-containing cosmetic carrier. Suitable water-containing cosmetic carriers are, for example, creams, emulsions, gels or even surfactant-containing foaming solutions, for example shampoos or other formulations suitable for application to the keratin-containing fibers. If necessary, the colorants may even be incorporated in water-free carriers.

The colorants according to the invention may also contain any of the known active substances, additives and auxiliaries typical of such formulations. In many cases, the colorants contain at least one surfactant, both anionic and zwitterionic, ampholytic, nonionic and cationic surfactants being suitable in principle. In many cases, however, it has been found to be of advantage to select the surfactants from anionic, zwitterionic or nonionic surfactants.

Suitable anionic surfactants for the compositions according to the invention are any anionic surface-active substances suitable for use on the human body. Such substances are characterized by a water-solubilizing anionic group such as, for example, a carboxylate, sulfate, sulfonate or phosphate group and a lipophilic alkyl group containing around 10 to 22 carbon atoms. In addition, glycol or polyglycol ether groups, ester, ether, amide groups and hydroxyl groups may also be present in the molecule.

5 The following are examples of suitable anionic surfactants - in the form of the sodium, potassium and ammonium salts and the mono-, di- and trialkanolammonium salts containing 2 or 3 carbon atoms in the alkanol group:

10 - linear fatty acids containing 10 to 22 carbon atoms (soaps),
- ether carboxylic acids corresponding to the formula $R-O-(CH_2-CH_2O)_x-CH_2-COOH$, in which R is a linear alkyl group containing 10 to 22 carbon atoms and $x = 0$ or 1 to 16,

15 - acyl sarcosides containing 10 to 18 carbon atoms in the acyl group,
- acyl taurides containing 10 to 18 carbon atoms in the acyl group,
- acyl isethionates containing 10 to 18 carbon atoms in the acyl group,
- sulfosuccinic acid mono- and dialkyl esters containing 8 to 18 carbon atoms in the alkyl group and sulfosuccinic acid monoalkyl polyoxyethyl esters containing 8 to 18 carbon atoms in the alkyl group and 1 to 6 oxyethyl groups,

20 - linear alkane sulfonates containing 12 to 18 carbon atoms,
- linear α -olefin sulfonates containing 12 to 18 carbon atoms,

25 - α -sulfofatty acid methyl esters of fatty acids containing 12 to 18 carbon atoms,
- alkyl sulfates and alkyl polyglycol ether sulfates corresponding to the formula $R-O(CH_2-CH_2O)_x-SO_3H$, in which R is a preferably linear alkyl group containing 10 to 18 carbon atoms and $x = 0$ or 1 to 12,

30 - mixtures of surface-active hydroxysulfonates according to **DE-A-37 25**

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- sulfated hydroxyalkyl polyethylene and/or hydroxyalkylene propylene glycol ethers according to **DE-A-37 23 354**,
- sulfonates of unsaturated fatty acids containing 12 to 24 carbon atoms and 1 to 6 double bonds according to **DE-A-39 26 344**,
- esters of tartaric acid and citric acid with alcohols in the form of addition products of around 2 to 15 molecules of ethylene oxide and/or propylene oxide with fatty alcohols containing 8 to 22 carbon atoms.

Preferred anionic surfactants are alkyl sulfates, alkyl polyglycol ether sulfates and ether carboxylic acids containing 10 to 18 carbon atoms in the alkyl group and up to 12 glycol ether groups in the molecule and, in particular, salts of saturated and, more particularly, unsaturated C₈₋₂₂ carboxylic acids, such as oleic acid, stearic acid, isostearic acid and palmitic acid.

In the context of the invention, zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group and at least one -COO⁽⁻⁾ or -SO₃⁽⁻⁾ group in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines, such as N-alkyl-N,N-dimethyl ammonium glycinate, for example coconutalkyl dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinate, for example coconutacylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group and coconutacylaminooethyl hydroxyethyl carboxymethyl glycinate. A preferred zwitterionic surfactant is the fatty acid amide derivative known by the CTFA name of Cocamidopropyl Betaine.

Ampholytic surfactants are surface-active compounds which, in addition to a C₈₋₁₈ alkyl or acyl group, contain at least one free amino group and at least one -COOH or -SO₃H group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants

are N-alkyl glycines, N-alkyl propionic acids, N-alkyl aminobutyric acids, N-alkyl iminodipropionic acids, N-hydroxyethyl-N-alkyl amidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkyl aminopropionic acids and alkyl aminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred amphotytic surfactants are N-coconutalkyl aminopropionate, coconutacyl aminoethyl aminopropionate and C₁₂₋₁₈ acyl sarcosine.

Nonionic surfactants contain, for example, a polyol group, a poly-alkylene glycol ether group or a combination of polyol and polyglycol ether groups as the hydrophilic group. Examples of such compounds are

- products of the addition of 2 to 30 moles of ethylene oxide and/or 0 to 5 moles of propylene oxide onto linear fatty alcohols containing 8 to 22 carbon atoms, onto fatty acids containing 12 to 22 carbon atoms and onto alkylphenols containing 8 to 15 carbon atoms in the alkyl group,
- C₁₂₋₂₂ fatty acid monoesters and diesters of products of the addition of 1 to 30 moles of ethylene oxide onto glycerol,
- C₈₋₂₂ alkyl mono- and oligoglycosides and ethoxylated analogs thereof,
- products of the addition of 5 to 60 moles of ethylene oxide onto castor oil and hydrogenated castor oil,
- products of the addition of ethylene oxide onto sorbitan fatty acid esters,
- products of the addition of ethylene oxide onto fatty acid alkanolamides.

Examples of cationic surfactants suitable for use in the hair treatment formulations according to the invention are, in particular, quaternary ammonium compounds. Preferred quaternary ammonium compounds are ammonium halides, such as alkyl trimethyl ammonium chlorides, dialkyl dimethyl ammonium chlorides and trialkyl methyl ammonium chlorides, for example cetyl trimethyl ammonium chloride, stearyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride, lauryl dimethyl ammonium chloride, lauryl dimethyl benzyl ammonium chloride and tricetyl methyl ammonium chloride. Other cationic

surfactants suitable for use in accordance with the invention are the quaternized protein hydrolyzates.

Also suitable for use in accordance with the invention are cationic silicone oils such as, for example, the commercially available products Q2-

5 7224 (manufacturer: Dow Corning; a stabilized trimethyl silyl amodimethicone), Dow Corning 929 Emulsion (containing a hydroxylamino-modified silicone which is also known as amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethyl siloxanes, quaternium-80).

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Alkyl amidoamines, particularly fatty acid amidoamines, such as the stearyl amidopropyl dimethyl amine obtainable as Tego Amid®S 18, are distinguished not only by their favorable conditioning effect, but also and in particular by their ready biodegradability.

15 Quaternary ester compounds, so-called "esterquats", such as the methyl hydroxyalkyl dialkoyloxyalkyl ammonium methosulfates marketed under the trade name of Stepantex®, are also readily biodegradable.

One example of a quaternary sugar derivative suitable for use as a cationic surfactant is the commercially available product Glucquat®100 (CTFA name: Lauryl Methyl Gluceth-10 Hydroxypropyl Dimonium Chloride).

The compounds containing alkyl groups used as surfactants may be single compounds. In general, however, these compounds are produced from native vegetable or animal raw materials so that mixtures with different alkyl chain lengths dependent upon the particular raw material are obtained.

The surfactants representing addition products of ethylene and/or propylene oxide with fatty alcohols or derivatives of these addition products may be both products with a "normal" homolog distribution and products with a narrow homolog distribution. Products with a "normal" homolog

distribution are mixtures of homologs which are obtained in the reaction of fatty alcohol and alkylene oxide using alkali metals, alkali metal hydroxides or alkali metal alcoholates as catalysts. By contrast, narrow homolog distributions are obtained when, for example, hydrotalcites, alkaline earth 5 metal salts of ether carboxylic acids, alkaline earth metal oxides, hydroxides or alcoholates are used as catalysts. The use of products with a narrow homolog distribution can be of advantage.

Other active substances, auxiliaries and additives are, for example,

- nonionic polymers such as, for example, vinyl pyrrolidone/vinyl acrylate 10 copolymers, polyvinyl pyrrolidone and vinyl pyrrolidone/vinyl acetate copolymers and polysiloxanes,
- cationic polymers, such as quaternized cellulose ethers, polysiloxanes containing quaternary groups, dimethyl diallyl ammonium chloride polymers, acrylamide/dimethyl diallyl ammonium chloride copolymers, 15 dimethyl aminoethyl methacrylate/vinyl pyrrolidone copolymers quaternized with diethyl sulfate, vinyl pyrrolidone/imidazolinium methochloride copolymers and quaternized polyvinyl alcohol,
- zwitterionic and amphoteric polymers such as, for example, acrylamido-propyl/trimethyl ammonium chloride/acrylate copolymers and octyl acrylamide/methyl methacrylate/tert.butyl aminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers,
- anionic polymers such as, for example, polyacrylic acids, crosslinked 20 polyacrylic acids, vinyl acetate/crotonic acid copolymers, vinyl pyrrolidone/vinyl acrylate copolymers, vinyl acetate/butyl maleate/isobornyl acrylate copolymers, methyl vinyl ether/maleic anhydride 25 copolymers and acrylic acid/ethyl acrylate/N-tert.butyl acrylamide terpolymers,
- thickeners, such as agar agar, guar gum, alginates, xanthan gum, gum arabic, karaya gum, locust bean gum, linseed gums, dextrans, cellulose 30 derivatives, for example methyl cellulose, hydroxyalkyl cellulose and

carboxymethyl cellulose, starch fractions and derivatives, such as amylose, amylopectin and dextrans, clays such as, for example, bentonite or fully synthetic hydrocolloids such as, for example, polyvinyl alcohol,

- structurants, such as glucose and maleic acid,
- hair-conditioning compounds, such as phospholipids, for example soya lecithin, egg lecithin and cephalins, and also silicone oils,
- protein hydrolyzates, more particularly elastin, collagen, keratin, milk protein, soya protein and wheat protein hydrolyzates, condensation products thereof with fatty acids and quaternized protein hydrolyzates,
- perfume oils, dimethyl isosorbide and cyclodextrins,
- solubilizers, such as ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol and diethylene glycol,
- antidandruff agents, such as Piroctone Olamine and Zinc Omadine,
- other substances for adjusting the pH value,
- active substances, such as panthenol, pantothenic acid, allantoin, pyrrolidone carboxylic acids and salts thereof, plant extracts and vitamins,
- cholesterol,
- UV filters,
- consistency factors, such as sugar esters, polyol esters or polyol alkyl ethers,
- fats and waxes, such as spermaceti, beeswax, montan wax, paraffins, fatty alcohols and fatty acid esters,
- fatty acid alkanolamides,
- complexing agents, such as EDTA, NTA and phosphonic acids,
- swelling and penetration agents, such as glycerol, propylene glycol monoethyl ether, carbonates, hydrogen carbonates, guanidines, ureas and primary, secondary and tertiary phosphates, imidazoles, tannins, pyrrole,

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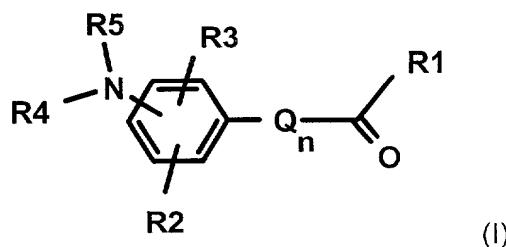
- opacifiers, such as latex,
- pearlizers, such as ethylene glycol mono- and distearate,
- propellents, such as propane/butane mixtures, N_2O , dimethyl ether, CO_2 and air and
- 5 - antioxidants.

To produce the colorants according to the invention, the constituents of the water-containing carrier are used in the usual quantities for this purpose. For example, emulsifiers are used in concentrations of 0.5 to 30% by weight while thickeners are used in concentrations of 0.1 to 25% by weight, based on the colorant as a whole.

It can be of advantage to the coloring result to add ammonium or metal salts to the colorants. Suitable metal salts are, for example, formates, carbonates, halides, sulfates, butyrates, valerates, caproates, acetates, lactates, glycolates, tartrates, citrates, gluconates, propionates, 15 phosphates and phosphonates of alkali metals, such as potassium, sodium or lithium, alkaline earth metals, such as magnesium, calcium, strontium or barium, or of aluminium, manganese, iron, cobalt, copper or zinc, sodium acetate, lithium bromide, calcium bromide, calcium gluconate, zinc chloride, zinc sulfate, magnesium chloride, magnesium sulfate, ammonium 20 carbonate, chloride and acetate being preferred. These salts are preferably present in a quantity of 0.03 to 65 mmol and more preferably in a quantity of 1 to 40 mmol, based on 100 g of the colorant as a whole.

The pH value of the ready-to-use coloring compositions is normally in the range from 2 to 12 and preferably in the range from 4 to 10.

25 The present invention also relates to the use of a combination of aromatic aldehydes or ketones corresponding to formula I:



in which

R^1 is a hydrogen atom, a C_{1-4} alkyl or an aryl group,

5 R^2 and R^3 independently of one another represent a hydrogen atom, a C_{1-4} alkyl group, a halogen atom, a hydroxy, C_{1-4} alkoxy or nitro group or together form a fused aromatic ring,

10 R^4 and R^5 represent a hydrogen atom, a C_{1-4} alkyl, C_{2-4} hydroxyalkyl, C_{1-4} alkenyl or aryl group or, together with the nitrogen atom, form a five- to

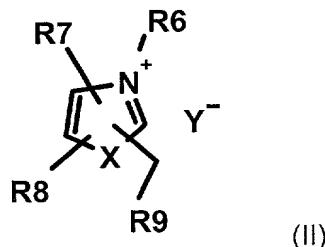
15 seven-membered heterocyclic ring or one of them forms a saturated or unsaturated 5-, 6- or 7-membered ring with one of the substituents R^2 or R^3 ,

Q is a direct bond or a vinylene or vinylidene group which, together with one of the two substituents R^4 or R^5 , may form an indole ring or - where an

15 exocyclic double bond is formed - an indoline ring and

$n = 1$ or 2 ,

and CH-active compounds corresponding to formulae II and/or III:



20

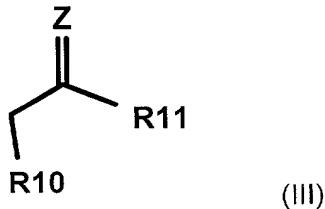
in which

R^6 is a C_{1-10} alkyl, C_{2-10} alkenyl, C_{2-4} hydroxyalkyl, C_{2-4} carboxyalkyl, C_{2-4}

sulfoalkyl or aralkyl group,

R⁷ and R⁸ independently of one another represent a hydrogen atom, a C₁₋₄ alkyl group, a halogen atom, a hydroxy, C₁₋₄ alkoxy or nitro group or together form a fused aromatic ring,

5 R⁹ represents a hydrogen atom, a C₁₋₄ alkyl or an aryl group,
 X is an oxygen or sulfur atom, the group >N-R¹² or -CH=CH-, where R¹² is a C₁₋₄ alkyl, C₂₋₄ carboxyalkyl, C₂₋₄ sulfoalkyl, C₂₋₄ sulfoxyalkyl, C₂₋₄ hydroxyalkyl or aralkyl group, and
 Y⁻ is an anion selected from halide, C₁₋₄ alkyl sulfate, C₁₋₄ alkane sulfonate,
 10 arene sulfonate, C₁₋₄ perfluoroalkanesulfonate, tetrafluoroborate, perhalogenate, sulfate, hydrogen sulfate or carboxylate,

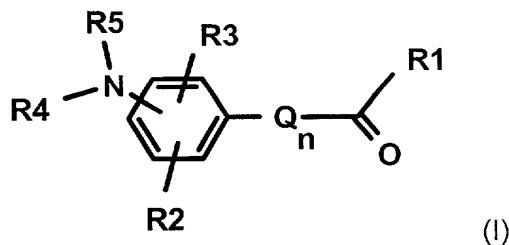


in which

R¹⁰ is a C₁₋₄ acyl group, aroyl, C₁₋₄ alkylsulfonyl, C₁₋₄ alkylsulfinyl, C₁₋₄ alkylamino, di-C₁₋₄-alkylamino, vinylcarbonyl, methineimino, nitrile, ester or carboxylic acid amide group which may optionally be substituted by C₁₋₄ alkyl, C₂₋₄ hydroxyalkyl or aryl groups and
 15 R¹¹ is a C₁₋₄ acyl, C₁₋₄ alkoxy, C₁₋₄ alkylamino, C₁₋₄ acylamino or di-C₁₋₄-alkylamino group,
 20 the substituents R¹⁰ and R¹¹ together with the rest of the molecule forming a 5-, 6- or 7-membered heterocycle from the series of 1,3-thiazolidine-2,5-diones, 1,3-thiazolidine-2-thione-5-ones, perhydropyrimidine-2,4,6-triones, perhydropyrimidine-2-thione-4,6-diones, cyclopentane-1,3-diones, cyclohexane-1,3-diones, indolines, indan-1,3-diones, indan-1-ones, 2-pyrazoline-5-ones, 1,2-dihydro-6-hydroxy-2-hydroxypyridines or enol esters thereof, and
 25 Z represents oxygen, sulfur or the dicyanomethylene group,

and/or reaction products of these compounds,
as a coloring component in oxidation hair colorants.

The present invention also relates to a process for coloring keratin-containing fibers, more particularly human hair, in which a colorant 5 containing a combination of aromatic aldehyde or ketones corresponding to formula I:



10 in which

R¹ is a hydrogen atom, a C₁₋₄ alkyl or an aryl group,

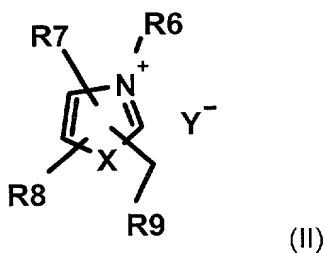
R² and R³ independently of one another represent a hydrogen atom, a C₁₋₄ alkyl group, a halogen atom, a hydroxy, C₁₋₄ alkoxy or nitro group or together form a fused aromatic ring,

15 R⁴ and R⁵ represent a hydrogen atom, a C₁₋₄ alkyl, C₂₋₄ hydroxyalkyl, C₁₋₄ alkenyl or aryl group or, together with the nitrogen atom, form a five- to seven-membered heterocyclic ring or one of them forms a saturated or unsaturated 5-, 6- or 7-membered ring with one of the substituents R² or R³,

20 Q is a direct bond or a vinylene or vinylidene group which, together with one of the two substituents R⁴ or R⁵, may form an indole ring or - where an exocyclic double bond is formed - an indoline ring and

n = 1 or 2,

and CH-active compounds corresponding to formulae II and/or III:



in which

R⁶ is a C₁₋₁₀ alkyl, C₂₋₁₀ alkenyl, C₂₋₄ hydroxyalkyl, C₂₋₄ carboxyalkyl, C₂₋₄ sulfoalkyl or aralkyl group,

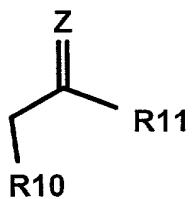
5 R⁷ and R⁸ independently of one another represent a hydrogen atom, a C₁₋₄ alkyl group, a halogen atom, a hydroxy, C₁₋₄ alkoxy or nitro group or together form a fused aromatic ring,

R⁹ represents a hydrogen atom, a C₁₋₄ alkyl or an aryl group,

X is an oxygen or sulfur atom, the group >N-R¹² or -CH=CH-, where R¹² is

10 a C₁₋₄ alkyl, C₂₋₄ carboxyalkyl, C₂₋₄ sulfoalkyl, C₂₋₄ sulfoxyalkyl, C₂₋₄ hydroxyalkyl or aralkyl group, and

Y⁻ is an anion selected from halide, C₁₋₄ alkyl sulfate, C₁₋₄ alkane sulfonate, arene sulfonate, C₁₋₄ perfluoroalkanesulfonate, tetrafluoroborate, perhalogenate, sulfate, hydrogen sulfate or carboxylate,



15

in which

R¹⁰ is a C₁₋₄ acyl group, aroyl, C₁₋₄ alkylsulfonyl, C₁₋₄ alkylsulfinyl, C₁₋₄ alkylamino, di-C₁₋₄-alkylamino, vinylcarbonyl, methineimino, nitrile, ester or carboxylic acid amide group which may optionally be substituted by C₁₋₄

20 alkyl, C₂₋₄ hydroxyalkyl or aryl groups and

R¹¹ is a C₁₋₄ acyl, C₁₋₄ alkoxy, C₁₋₄ alkylamino, C₁₋₄ acylamino or di-C₁₋₄-alkylamino group,

the substituents R¹⁰ and R¹¹ together with the rest of the molecule forming

a 5-, 6- or 7-membered heterocycle from the series of 1,3-thiazolidine-2,5-diones, 1,3-thiazolidine-2-thione-5-ones, perhydropyrimidine-2,4,6-triones, perhydropyrimidine-2-thione-4,6-diones, cyclopentane-1,3-diones, cyclohexane-1,3-diones, indolines, indan-1,3-diones, indan-1-ones, 2-pyrazoline-5-ones, 1,2-dihydro-6-hydroxy-2-hydroxypyridines or enol esters thereof, and

Z represents oxygen, sulfur or the dicyanomethylene group, and/or reaction products of these compounds and typical cosmetic ingredients is applied to the keratin-containing fibers, left thereon for a 10 while, usually about 30 minutes, and then rinsed out or washed out with a shampoo.

The aromatic aldehydes or ketones corresponding to formula I and the CH-active compounds corresponding to formula II and/or III may be applied to the hair either simultaneously or successively; in the latter case, 15 it does not matter which of the two components is applied first. The ammonium or metal salts optionally present may be added to the first component or to the second component. A period of up to 30 minutes may elapse between application of the first component and the second component. The fibers may also be pretreated with the salt solution.

20 The aromatic aldehydes or ketones corresponding to formula I and the CH-active compounds corresponding to formulae II and/or III may be stored either separately or together either in a liquid or paste-form preparation (water-based or water-free) or as a dry powder. In the event of separate storage, the components are thoroughly mixed together just 25 before application. In the event of dry storage, a certain quantity of warm (30 to 80°C) water is normally added and a homogeneous mixture prepared before application.

Examples**Preparation of a coloring solution:**

Suspensions of 5 mmol of an aromatic aldehyde or ketone
5 corresponding to formula I and 5 mmol of a CH-active compound
corresponding to formula II or III in 25 ml of water at 60°C were prepared.
After cooling to 30°C, the suspensions were mixed together, 5 mmol of
sodium acetate, optionally 5 mmol of piperidine and one drop of a 20%
fatty alkyl ether sulfate solution were added and the pH was adjusted
10 accordingly with dilute NaOH or hydrochloric acid.

Where reaction products of the compounds of formula I and
compounds of formula II or III were used, 5 mmol of the reaction product
was suspended or dissolved in 50 ml of water.

A tress of 90% grey, non-pretreated human hair was placed in this
15 coloring solution for 30 minutes at 30°C. The tress was then rinsed for 30
seconds with luke-warm water, dried with warm air and then combed out.

The particular shades and depths of color are shown in the following
Tables.

The depth of color was evaluated on the following scale:

20 - : very faint, if any, color
 (+) : weak intensity
 + : medium intensity
 +(+) : medium to strong intensity
 ++ : strong intensity
 ++(+) : strong to very strong intensity
 +++ : very strong intensity

Table 1

Aromatic aldehyde or ketone	Compound of formula II or III	Color intensifier	pH	Color	Intensity
4-Dimethylamino-benzaldehyde	1-Ethyl-2-methyl quinolinium iodide	Piperidine	9.0	Violet-red	++(+)
4-Dimethylamino-benzaldehyde	1,4-Dimethyl quinolinium methane sulfonate	Piperidine	9.0	Red-violet	+(+)
4-Dimethylamino-benzaldehyde	3-Ethyl-2-methylbenzo-thiazolium-p-toluene-sulfonate	Piperidine	7.60	Bright pinky red	+++
4-Dimethylamino-benzaldehyde	Rhodanine	Piperidine	7.60	Bright orange	++(+)
4-Dimethylamino-benzaldehyde	Oxindole	Piperidine	9.00	Gold-yellow	++(+)
4-Dimethylamino-benzaldehyde	1,3-Diethylthiobarbituric acid	--	9.00	Orange	++
4-Dimethylamino-benzaldehyde	1-Ethyl-2-methylnaphtho-[1,2-d]-thiazolium-p-toluenesulfonate	--	6.00	Carmine red	++(+)
4-Dimethylamino-1-naphthaldehyde	1-Ethyl-2-methylnaphtho-[1,2-d]-thiazolium-p-toluenesulfonate	--	6.00	Dark violet	++(+)

Table 1 continued

Aromatic aldehyde or ketone	Compound of formula II or III	Color intensifier	pH	Color	Intensity
4-Dimethylamino-1-naphthaldehyde	3-Ethyl-2-methylbenzothiazolium-p-toluenesulfonate	Piperidine	7.73	Red violet	++(+)
4-Dimethylamino-1-naphthaldehyde	1-Ethyl-2-methyl quinolinium iodide	Piperidine	9.00	Violet-brown	+(+)
4-Dimethylamino-cinnamaldehyde	1-Ethyl-2-methyl quinolinium iodide	Piperidine	9.00	Dark orange-brown	++(+)
4-Dimethylamino-cinnamaldehyde	3-Ethyl-2-methylbenzothiazolium-p-toluenesulfonate	Piperidine	7.33	Brown	++
4-Dimethylamino-cinnamaldehyde	Rhodanine	--	6.00	Red-orange	++
4-Dimethylamino-cinnamaldehyde	Rhodanine acetic acid	--	6.00	Orange-red	++(+)
4-Dimethylamino-cinnamaldehyde	1,3-Diethyl thiobarbituric acid	--	9.00	Brown-violet	++
4-Dimethylamino-cinnamaldehyde	1,4-Dimethyl quinolinium methane sulfonate	Piperidine	9.00	Dark yellow-brown	++

Table 1 continued

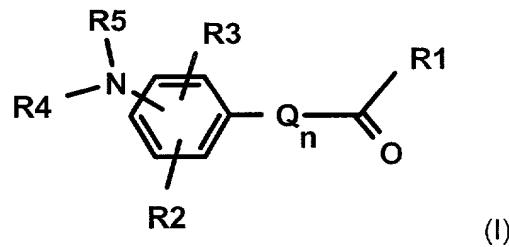
Aromatic aldehyde or ketone	Compound of formula II or III	Color intensifier	pH	Color	Intensity
1,3,3-Trimethyl-2-formylmethylen indoline (tribase aldehyde)	1,4-Dimethylquinolinium methanesulfonate	Piperidine	9.00	Grey-green	+
Tribase aldehyde	3-Ethyl-2-methylbenzoxazolium iodide	--	6.00	Pinky red	+
Tribase aldehyde	3-Ethyl-2-methylbenzoxazolium iodide	Piperidine	9.00	Dark pinky red	++(+)
Tribase aldehyde	3-Ethyl-2-methylbenzothiazolium-p-toluenesulfonate	Piperidine	8.50	Pinky red (pink)	++
Tribase aldehyde	3-Ethyl-2-methylnaphtho[1,2-d]-thiazolium-p-toluenesulfonate	--	7.27	Violet-orange	+
1-Methylindole-3-aldehyde	1-Ethyl-2-methylnaphtho[1,2-d]-thiazolium-p-toluenesulfonate	--	6.00	Red-orange	++(+)
Indole-3-aldehyde	1-Ethyl-2-methylnaphtho[1,2-d]-thiazolium-p-toluenesulfonate	--	6.00	Yellow-orange	+
Indole-3-aldehyde	3-Ethyl-2-methylbenzothiazolium iodide	--	6.00	Gold-yellow	+

Table 2Coloring with reaction products of compounds I and II

Reaction product	Color	Intensity	pH
2-(4-Dimethylaminostyryl)-1-ethylpyridinium iodide	Bright orange	+++	6.00
2-(4-Dimethylaminostyryl)-1-methyl quinolinium iodide	Violet-red	++(+)	6.00
4-[(1-methyl-4(1H)-pyridinylidene]-ethylidene-2,5-cyclohexadien-1-one	Orange-yellow	+(+)	6.00
3-(4-Dimethylaminobenzylidene)-2-indolinone	Gold-yellow	++	6.00
5-(4-Dimethylaminobenzylidene)-5-thioxo-2-pyrrolidinone	Bright orange	++	6.00
2-(4-Dimethylaminostyryl)-3-ethyl benzothiazolium iodide	Bright orange	++	6.00

CLAIMS

1. A composition for coloring keratin-containing fibers, more particularly human hair, containing as a coloring component a combination of aromatic aldehydes or ketones corresponding to formula I:



5

in which

R^1 is a hydrogen atom, a C_{1-4} alkyl or an aryl group,

R^2 and R^3 independently of one another represent a hydrogen atom, a C_{1-4}

10 alkyl group, a halogen atom, a hydroxy, C_{1-4} alkoxy or nitro group or together form a fused aromatic ring,

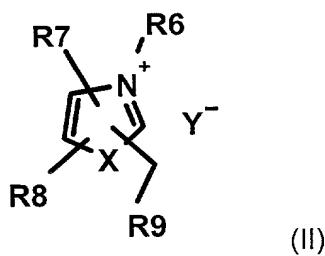
R^4 and R^5 represent a hydrogen atom, a C_{1-4} alkyl, C_{2-4} hydroxyalkyl, C_{1-4} alkenyl or aryl group or, together with the nitrogen atom, form a five- to seven-membered heterocyclic ring or one of them forms a saturated or 15 unsaturated 5-, 6- or 7-membered ring with one of the substituents R^2 or R^3 ,

Q is a direct bond or a vinylene or vinylidene group which, together with one of the two substituents R^4 or R^5 , may form an indole ring or - where an exocyclic double bond is formed - an indoline ring and

20 $n = 1$ or 2,

and CH-active compounds corresponding to formulae II and/or III:

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in which

R⁶ is a C₁₋₁₀ alkyl, C₂₋₁₀ alkenyl, C₂₋₄ hydroxyalkyl, C₂₋₄ carboxyalkyl, C₂₋₄

5 sulfoalkyl or aralkyl group,

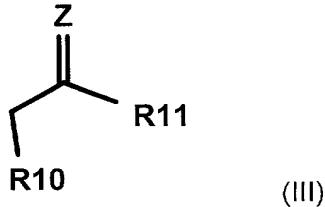
R⁷ and R⁸ independently of one another represent a hydrogen atom, a C₁₋₄ alkyl group, a halogen atom, a hydroxy, C₁₋₄ alkoxy or nitro group or together form a fused aromatic ring,

R⁹ represents a hydrogen atom, a C₁₋₄ alkyl or an aryl group,

10 X is an oxygen or sulfur atom, the group >N-R¹² or -CH=CH-, where R¹² is a C₁₋₄ alkyl, C₂₋₄ carboxyalkyl, C₂₋₄ sulfoalkyl, C₂₋₄ sulfoxyalkyl, C₂₋₄ hydroxyalkyl or aralkyl group, and

Y- is an anion selected from halide, C₁₋₄ alkyl sulfate, C₁₋₄ alkane sulfonate, arene sulfonate, C₁₋₄ perfluoroalkanesulfonate, tetrafluoroborate,

15 perhalogenate, sulfate, hydrogen sulfate or carboxylate,



in which

R¹⁰ is a C₁₋₄ acyl group, aroyl, C₁₋₄ alkylsulfonyl, C₁₋₄ alkylsulfinyl, C₁₋₄ alkylamino, di-C₁₋₄-alkylamino, vinylcarbonyl, methineimino, nitrile, ester or

20 carboxylic acid amide group which may optionally be substituted by C₁₋₄ alkyl, C₂₋₄ hydroxyalkyl or aryl groups and

R¹¹ is a C₁₋₄ acyl, C₁₋₄ alkoxy, C₁₋₄ alkylamino, C₁₋₄ acylamino or di-C₁₋₄-alkylamino group,

the substituents R¹⁰ and R¹¹ together with the rest of the molecule forming a 5-, 6- or 7-membered heterocycle from the series of 1,3-thiazolidine-2,5-diones, 1,3-thiazolidine-2-thione-5-ones, perhydropyrimidine-2,4,6-triones, perhydropyrimidine-2-thione-4,6-diones, cyclopentane-1,3-diones, 5 cyclohexane-1,3-diones, indoles, indan-1,3-diones, indan-1-ones, 2-pyrazoline-5-ones, 1,2-dihydro-6-hydroxy-2-hydroxypyridines or enol esters thereof, and

Z represents oxygen, sulfur or the dicyanomethylene group, and/or reaction products of these compounds.

2. A composition as claimed in claim 1, characterized in that 4-dimethylaminobenzaldehyde, 4-diethylaminobenzaldehyde, 4-dimethylamino-2-hydroxybenzaldehyde, 4-pyrrolidinobenzaldehyde, 4-morpholinobenzaldehyde, 4-piperidinobenzaldehyde, 4-dimethylaminoacetophenone, 4-dimethylaminonaphthaldehyde, 4-dimethylaminobenzylidene acetone, 4-dimethylamino cinnamaldehyde, 2-dimethylaminobenzaldehyde, 2-chloro-4-dimethylaminobenzaldehyde, 4-dimethylamino-2-methylbenzaldehyde, trans-4-diethylaminocinnamaldehyde, 4-(dibutylamino)-benzaldehyde, 4-diphenylaminobenzaldehyde, 2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinoxiline-9-carboxaldehyde, 4-dimethylamino-2-methoxybenzaldehyde, 2,3,6,7-tetrahydro-8-hydroxy-1H,5H-benzo[ij]quinoxiline-9-carboxaldehyde, 4-(1-imidazolyl)-benzaldehyde, 2-morpholinobenzaldehyde, indole-3-carboxaldehyde, 1-methylindole-3-carboxaldehyde, N-ethylcarbazole-3-aldehyde, 2-formylmethylene-1,3,3-trimethylindoline (Fischer's aldehyde or tribase aldehyde) and mixtures thereof are used as the compounds of formula I.

3. A composition as claimed in claim 1 or 2, characterized in that 1,4-dimethylquinolinium, 1,2-dimethylquinolinium, 1,4-dimethylpyridinium, 1,2-dimethylpyridinium, 2-methyl-1-ethylquinolinium, 2,3-dimethylisoquinolinium, 1,2,3,3-tetramethyl-3H-indolinium, 2,3-dimethylbenzothiazolium, 2,3-dimethyl-6-nitrobenzothiazolium, 3-benzyl-2-benzothiazolium, 2-methyl-3-

propyl benzothiazolium, 2,4-dimethyl-3-ethylthiazolium, 3-(2-carboxyethyl)-2,5-dimethylbenzothiazolium, 1,2,3-trimethylbenzimidazolium, 5,6-dichloro-1,3-diethyl-2-methyl benzimidazolium, 3-ethyl-2-methylbenzothiazolium, 3-ethyl-2-methylnaphtho[1,2-d]thiazolium, 5-chloro-3-ethyl-2-methylbenzothiazolium, 3-ethyl-2-methyl benzoxazolium salts which may be present, for example, as chlorides, bromides, iodides, methanesulfonates, benzenesulfonates, p-toluenesulfonates, trifluoromethane sulfonates, methyl sulfates, tetrafluoroborates and 2-methyl-3-(3-sulfopropyl)-benzothiazolium hydroxide, inner salt, 5-methoxy-2-methyl-3-(3-sulfopropyl)-benzothiazolium hydroxide, inner salt and mixtures of the above are used as the compounds of formula II.

4. A composition as claimed in any of claims 1 to 3, characterized in that rhodanine, rhodanine-3-acetic acid, barbituric acid, thiobarbituric acid, 1,3-dimethyl and 1,3-diethyl thiobarbituric acid, oxindole, 3-indoxyl acetate, coumaranone, 1-methyl-3-phenylpyrazolinone, indan-1,3-dione, cyclopentane-1,3-dione, 1,2-dihydro-1-ethyl-6-hydroxy-4-methyl-2-oxo-3-pyridinecarbonitrile and mixtures of the above are used as the compounds of formula III.

5. A composition as claimed in any of claims 1 to 4, characterized in that the reaction products of the compounds corresponding to formulae I and II and/or III are selected from Quinaldine Red (2-[4-(dimethylamino)-styryl]-1-ethyl quinolinium iodide), 2-[4-(dimethylamino)-styryl]-1-methyl quinolinium iodide, 2-[4-(dimethylamino)-styryl]-1-ethylpyridinium iodide, 2-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide, 4-[4-dimethylaminostyryl]-1-methyl pyridinium tosylate, 4-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizin-9-yl)-ethenyl]-1-methylpyridinium iodide, trans-4-[4-(dibutylamino)-styryl]-1-methyl pyridinium iodide and 2,6-bis-[4-(dimethylamino)-styryl]-1-methylpyridinium iodide, 2-[4-(dimethylamino)-styryl]-3-methyl benzoxazolium perchlorate, 2-[4-(dimethylamino)-styryl]-3-methyl benzoxazolium iodide, 2-[4-(dimethylamino)-styryl]-1-

ethylnaphthal[1,2-d]thiazolium iodide and mixtures of the above.

6. A composition as claimed in any of claims 1 to 5, characterized in that the aromatic aldehydes or ketones corresponding to formula I and the quaternary heterocyclic compounds corresponding to formula II and the CH-active compounds corresponding to formula III are used in quantities of 0.03 to 65 mmol and more particularly 1 to 40 mmol, based on 100 g of the colorant as a whole.

7. A composition as claimed in any of claims 1 to 6, characterized in that it contains color intensifiers selected from the group consisting of piperidine, piperidine-2-carboxylic acid, piperidine-3-carboxylic acid, piperidine-4-carboxylic acid, pyridine, 2-hydroxypyridine, 3-hydroxypyridine, 4-hydroxypyridine, imidazole, 1-methyl imidazole, histidine, pyrrolidine, proline, pyrrolidone, pyrrolidone-5-carboxylic acid, pyrazole, 1,2,4-triazole, piperazidine or mixtures thereof.

8. A composition as claimed in any of claims 1 to 7, characterized in that it contains substantive dyes from the group of nitrophenylenediamines, nitroaminopenols, anthraquinones or indophenols, preferably in a quantity of 0.01 to 20% by weight, based on the colorant as a whole.

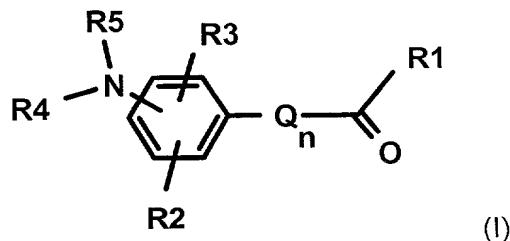
9. A composition as claimed in any of claims 1 to 8, characterized in that ammonium or metal salts selected from the group of formates, carbonates, halides, sulfates, butyrates, valerates, caproates, acetates, lactates, glycolates, tartrates, citrates, gluconates, propionates, phosphates and phosphonates of alkali metals, such as potassium, sodium or lithium, alkaline earth metals, such as magnesium, calcium, strontium or barium, or of aluminium, manganese, iron, cobalt, copper or zinc are added.

10. A composition as claimed in any of claims 1 to 9, characterized in that it contains oxidizing agents, more particularly H_2O_2 , in a quantity of 0.01 to 6% by weight, based on the solution applied.

11. A composition as claimed in any of claims 1 to 10, characterized in that it contains anionic, zwitterionic or nonionic surfactants.

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12. The use of a combination of aromatic aldehydes or ketones corresponding to formula I:



5

in which

R¹ is a hydrogen atom, a C₁₋₄ alkyl or an aryl group,

R² and R³ independently of one another represent a hydrogen atom, a C₁₋₄ alkyl group, a halogen atom, a hydroxy, C₁₋₄ alkoxy or nitro group or

10 together form a fused aromatic ring,

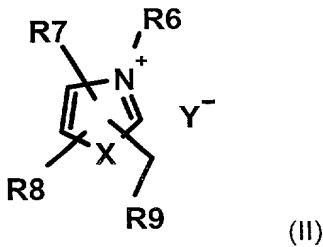
R⁴ and R⁵ represent a hydrogen atom, a C₁₋₄ alkyl, C₂₋₄ hydroxyalkyl, C₁₋₄ alkenyl or aryl group or, together with the nitrogen atom, form a five- to seven-membered heterocyclic ring or one of them forms a saturated or unsaturated 5-, 6- or 7-membered ring with one of the substituents R² or

15 R³,

Q is a direct bond or a vinylene or vinylidene group which, together with one of the two substituents R⁴ or R⁵, may form an indole ring or - where an exocyclic double bond is formed - an indoline ring and

n = 1 or 2,

20 and CH-active compounds corresponding to formulae II and/or III:



in which

R^6 is a C_{1-10} alkyl, C_{2-10} alkenyl, C_{2-4} hydroxyalkyl, C_{2-4} carboxyalkyl, C_{2-4} sulfoalkyl or aralkyl group,

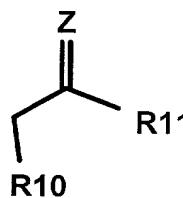
5 R^7 and R^8 independently of one another represent a hydrogen atom, a C_{1-4} alkyl group, a halogen atom, a hydroxy, C_{1-4} alkoxy or nitro group or together form a fused aromatic ring,

R^9 represents a hydrogen atom, a C_{1-4} alkyl or an aryl group,

X is an oxygen or sulfur atom, the group $>N-R^{12}$ or $-CH=CH-$, where R^{12} is

10 a C_{1-4} alkyl, C_{2-4} carboxyalkyl, C_{2-4} sulfoalkyl, C_{2-4} sulfoxyalkyl, C_{2-4} hydroxyalkyl or aralkyl group, and

Y^- is an anion selected from halide, C_{1-4} alkyl sulfate, C_{1-4} alkane sulfonate, arene sulfonate, C_{1-4} perfluoroalkanesulfonate, tetrafluoroborate, perhalogenate, sulfate, hydrogen sulfate or carboxylate,



15 (III)

in which

R^{10} is a C_{1-4} acyl group, aroyl, C_{1-4} alkylsulfonyl, C_{1-4} alkylsulfinyl, C_{1-4} alkylamino, di- C_{1-4} -alkylamino, vinylcarbonyl, methineimino, nitrile, ester or carboxylic acid amide group which may optionally be substituted by C_{1-4}

20 alkyl, C_{2-4} hydroxyalkyl or aryl groups and

R^{11} is a C_{1-4} acyl, C_{1-4} alkoxy, C_{1-4} alkylamino, C_{1-4} acylamino or di- C_{1-4} -alkylamino group,

the substituents R^{10} and R^{11} together with the rest of the molecule forming a 5-, 6- or 7-membered heterocycle from the series of 1,3-thiazolidine-2,5-

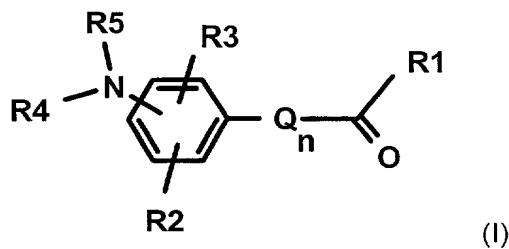
25 diones, 1,3-thiazolidine-2-thione-5-ones, perhydropyrimidine-2,4,6-triones, perhydropyrimidine-2-thione-4,6-diones, cyclopentane-1,3-diones, cyclohexane-1,3-diones, indolines, indan-1,3-diones, indan-1-ones, 2-

pyrazoline-5-ones, 1,2-dihydro-6-hydroxy-2-hydroxypyridines or enol esters thereof, and

Z represents oxygen, sulfur or the dicyanomethylene group, and/or reaction products of these compounds,

5 as a coloring component in oxidation hair colorants.

13. A process for coloring keratin-containing fibers, more particularly human hair, in which a colorant containing a combination of aromatic aldehyde or ketones corresponding to formula I:



10

in which

R¹ is a hydrogen atom, a C₁₋₄ alkyl or an aryl group,

R² and R³ independently of one another represent a hydrogen atom, a C₁₋₄

15 alkyl group, a halogen atom, a hydroxy, C₁₋₄ alkoxy or nitro group or together form a fused aromatic ring,

R⁴ and R⁵ represent a hydrogen atom, a C₁₋₄ alkyl, C₂₋₄ hydroxyalkyl, C₁₋₄ alkenyl or aryl group or, together with the nitrogen atom, form a five- to seven-membered heterocyclic ring or one of them forms a saturated or

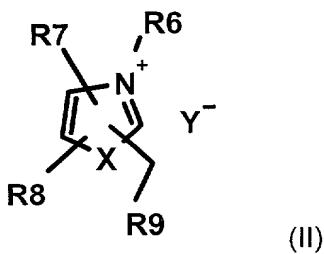
20 unsaturated 5-, 6- or 7-membered ring with one of the substituents R² or R³,

Q is a direct bond or a vinylene or vinylidene group which, together with one of the two substituents R⁴ or R⁵, may form an indole ring or - where an exocyclic double bond is formed - an indoline ring and

25 n = 1 or 2,

and CH-active compounds corresponding to formulae II and/or III:

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in which

R^6 is a C_{1-10} alkyl, C_{2-10} alkenyl, C_{2-4} hydroxyalkyl, C_{2-4} carboxyalkyl, C_{2-4} sulfoalkyl or aralkyl group,

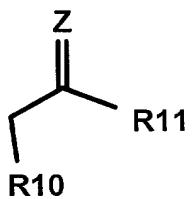
5 R^7 and R^8 independently of one another represent a hydrogen atom, a C_{1-4} alkyl group, a halogen atom, a hydroxy, C_{1-4} alkoxy or nitro group or together form a fused aromatic ring,

R^9 represents a hydrogen atom, a C_{1-4} alkyl or an aryl group,

X is an oxygen or sulfur atom, the group $>N-R^{12}$ or $-CH=CH-$, where R^{12} is

10 a C_{1-4} alkyl, C_{2-4} carboxyalkyl, C_{2-4} sulfoalkyl, C_{2-4} sulfoxyalkyl, C_{2-4} hydroxyalkyl or aralkyl group, and

Y^- is an anion selected from halide, C_{1-4} alkyl sulfate, C_{1-4} alkane sulfonate, arene sulfonate, C_{1-4} perfluoroalkanesulfonate, tetrafluoroborate, perhalogenate, sulfate, hydrogen sulfate or carboxylate,



15

in which

R^{10} is a C_{1-4} acyl group, aroyl, C_{1-4} alkylsulfonyl, C_{1-4} alkylsulfinyl, C_{1-4} alkylamino, di- C_{1-4} -alkylamino, vinylcarbonyl, methineimino, nitrile, ester or carboxylic acid amide group which may optionally be substituted by C_{1-4}

20 alkyl, C_{2-4} hydroxyalkyl or aryl groups and

R^{11} is a C_{1-4} acyl, C_{1-4} alkoxy, C_{1-4} alkylamino, C_{1-4} acylamino or di- C_{1-4} -alkylamino group,

the substituents R^{10} and R^{11} together with the rest of the molecule forming

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a 5-, 6- or 7-membered heterocycle from the series of 1,3-thiazolidine-2,5-diones, 1,3-thiazolidine-2-thione-5-ones, perhydropyrimidine-2,4,6-triones, perhydropyrimidine-2-thione-4,6-diones, cyclopentane-1,3-diones, cyclohexane-1,3-diones, indolines, indan-1,3-diones, indan-1-ones, 2-pyrazoline-5-ones, 1,2-dihydro-6-hydroxypyridines or enol esters thereof, and

Z represents oxygen, sulfur or the dicyanomethylene group, and/or reaction products of these compounds and typical cosmetic ingredients is applied to the keratin-containing fibers, left thereon for a while, usually about 30 minutes, and then rinsed out or washed out with a shampoo.

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(12) NACH DEM VERTRÄG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES
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A1

(54) Title: AGENT FOR DYING KERATIN FIBERS

(54) Bezeichnung: MITTEL ZUM FÄRBEN VON KERATINHALTIGEN FASERN

(57) Abstract: The invention relates to an agent for dyeing keratin fibers, especially human hair. Said agent contains at least one combination comprised of aromatic aldehydes or ketones and of CH-active compounds.

(57) Zusammenfassung: Es wird ein Mittel zum Färben von keratinhaltigen Fasern, insbesondere menschlichen Haaren, beansprucht, enthaltend mindestens eine Kombination aus aromatischen Aldehyden bzw. Ketonen und CH-aktiven Verbindungen.

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DECLARATION

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I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365© of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code §112.1 acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
	PCT/EP00/07163	08/02/2000	

Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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List Attorney(s) and/or agent(s) name and registration number below:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor:		<input type="checkbox"/> A petition has been filed for this unsigned inventor				
Given <u>H. Hinrich</u> Name		Middle Initial	Family Name	<u>Moeller</u>		Suffix e.g. Jr.
Inventor's Signature	<u>Hinrich Moeller</u>				Date	9.04.02
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Post Office Address						
City	40789 Monheim	State	Zip	Country	Germany	Applicant Authority
<input checked="" type="checkbox"/> Additional inventors are being named on supplemental sheet(s) attached hereto						

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DECLARATION

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